Lithium Intercalation/Deintercalation in Cobalt Doped Lithium Nickel Oxide Dependence on Charge Cut-off Voltage

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Lithium nickel oxide ($LiNiO_2$) is a very promising cathode material in lithium battery because of lower cost and higher initial capacity compared to $LiCoO_2$. $LiNiO_2$, however, has several problems for lithium intercalation. One is the serious phase transition from hexagonal through monoclinic to other hexagonal during lithium intercalation/deintercalation between 3.0 and 4.3V. The partial substitution of Ni with Co can stabilize the lithium nickel oxide structure on cycling[1,2]. In this work, we investigated the charge/discharge behavior and capacity fade of $LiNi_{0.8}Co_{0.2}O_2$ on cycling while the charge cut-off voltage was varied from 3.9V to 4.5V vs. Li.

The $LiNi_{0.8}Co_{0.2}O_2$ electrodes were used as received from PolyStor Corp. as a part of our Advanced Technology Development program. They are coated with 1.8 mAh/cm^2 on one side of the Al foil current collectors. Other properties described in detail elsewhere[3]. One cm^2 disks were cut and assembled into metal Swagelok cells with Celgard separator, LP40 electrolyte (1M $LiPF_6$ /EC/DEC) and lithium foil counter electrodes.

Fig 1 shows the variation in shape of the initial cyclic voltammograms with charge cut-off voltage for the $LiNi_{0.8}Co_{0.2}O_2$ electrodes at 0.1mV/s scan rate. There are three peaks from 3.7V to 4.3V. During lithium intercalation/deintercalation, $LiNiO_2$ shows two significant phase transitions (hexagonal (H_1) to monoclinic (M) and monoclinic (M) to other hexagonal (H_2)), while $LiNi_{0.8}Co_{0.2}O_2$ showed a single hexagonal phase(H_1) from 3.6 to 4.08V. The hexagonal structure of $LiNi_{0.8}Co_{0.2}O_2$ transforms to the other hexagonal (H_2) form at around 4.2V[4]. In Fig. 1, the CV curve between 3.0 and 4.1V shows two peaks without phase transition.

Fig. 2 shows the discharge capacity of $LiNi_{0.8}Co_{0.2}O_2$ at various C rates up to 100 cycles. These cells were charged to voltages from 4.1V to 4.5V and discharged to 3.0V. The initial capacity of cell charged to 4.5V is higher than that charged to 4.1V. However, cell charged to 4.5V shows serious capacity fading at the 2C rate. After 25 cycles, the capacity of both cells decreased slightly on cycling and the capacity fading of cell charged to 4.5V is higher than that to 4.1V. If $LiNi_{0.8}Co_{0.2}O_2$ is charged and discharged to 4.5V, one of the reasons for capacity fading may be the phase transition from hexagonal (H_1) to other hexagonal (H_2) phase during the intercalation/deintercalation of lithium. Particle fracture of $LiNi_{0.8}Co_{0.2}O_2$ may also be occurring for charging potentials greater than 4.2V[5].

We also investigated the electrochemical and charging/discharging characteristics of aluminum doped lithium nickel cobalt oxide($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$).

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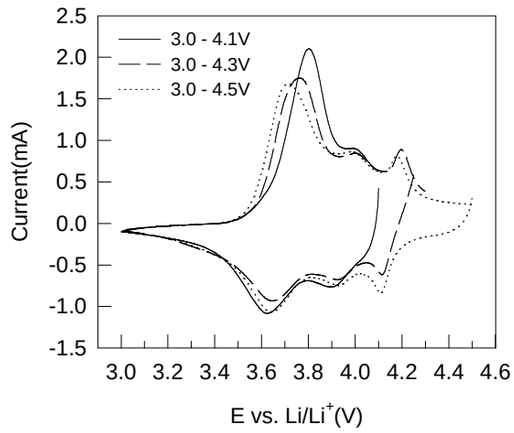

Fig. 1 Cyclic voltammograms of $LiNi_{0.8}Co_{0.2}O_2$ on cutoff voltage. Scan rate 0.1mV/s. Reference electrode and counter electrode : lithium foil. Electrode area 1 cm^2.

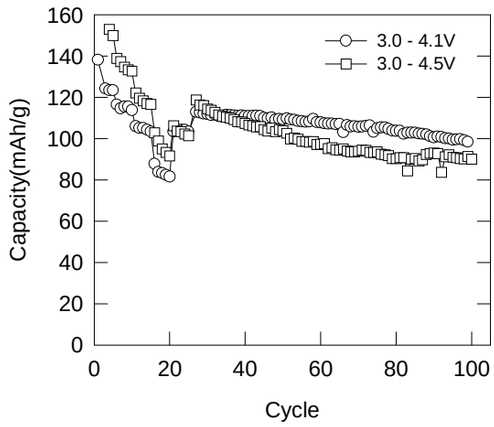

Fig. 2 Discharge capacity of $LiNi_{0.8}Co_{0.2}O_2$. First cycle C/25, 2nd-5th C/4, 6th-10th C/2, 11th-15th C/1, 16th-20th 2C, 21st-25th C/1 and 26th-100th C/2.